Relationship between dynamic heterogeneity and medium-range crystalline order

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多分散コロイド系におけるガラス転移現象を、計算機シミュレーションを用いて研究を進めてきた。その結果、過冷却液体中に中距離結晶秩序が形成されていることを確認した。さらに、この結晶秩序を形成している粒子のダイナミクスは、秩序を形成していない他の粒子に比べ遅いことを見出した。またこの中距離結晶秩序は、粒子の並進緩和時間の10倍程度の寿命をもち、この時間スケールを越えると各粒子のダイナミクスは、ほぼ均一になることも明らかとなった。以上より、我々は、中距離結晶秩序の存在がガラスの動的不均一性の起源であるという見解を得た。

Upon cooling, some liquids do not clystallize below the melting point, but instead become a glass at the glass transition temperature T_g. The most remarkable characteristic of the glass transition is that the dynamics of the liquids becomes significantly slower toward T_g with keeping its amorphous structure. Although many theoretical and numerical studies have been devoted to the origin of the glass transition, it remains unclear. Recently some study reported the existence of the dynamic heterogeneity in a glassy state and claimed that it might play a very important role in liquid-glass transition [1, 2]. Further some experimental and numerical studies reported that the cluster of the medium-range crystalline order does exist in a supercooled liquid state [3, 4]. Here we study the relationship between the dynamic heterogeneity and medium-range crystalline order by means of 2D Brownian dynamics simulation of polydisperse colloidal dispersion.

Polydisperse colloidal dispersion have attracted considerable interests as a model glass-forming liquid [5]. For a monodisperse system, a system just crystalinzes from a liquid state as the volume fraction of colloidal particle, ϕ, increases. On the other hand, a system of a high polydispersity does not crystallize even for large ϕ, and intead its dynamics slows down with the increasing ϕ. In other words, it enters a disordered glassy state. Since the polydispersity is regarded as the frustration upon the crystallization of liquids, we can control the glass-forming ability of a colloidal system by changing the degree of polydispersity. In our simulations, colloidal particles interact repulsively with each other as

$$U(r_{ij}) = \begin{cases} 4\epsilon\left\{\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6} + \frac{1}{4}\right\} & (\text{for } 0 < r_{ij} < 2^{\frac{1}{6}}\sigma_{ij}) \\ 0 \quad (\text{otherwise}) \end{cases} \tag{1}$$

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where $r_{ij} = |\vec{r}_i - \vec{r}_j|$, $\vec{r}_i$ is the position of particle i. $\sigma_{ij} = (R_i + R_j)/2$, where R_i is the diameter of particle i given by Gaussian distribution whose polydispersity is defined as $\Delta\sigma = \sqrt{\sum_i (R_i - \bar{R})^2/(N_p - 1)}$, where $\bar{R}$ is the average of the particle radii and N_p is the particle number.

Our simulations revealed the existence of the medium-range crystalline order in supercooled liquid states of the polydisperse colloidal dispersions by calculating the six-fold positional order Ψ_6. The six-fold positional order Ψ_6 is given as

$$(\Psi_6)_i = \frac{2}{n(n-1)} \sum_{k=1}^{n} \sum_{l=k+1}^{n} e^{6j\theta_{ikl}}, \tag{2}$$

where $j = \sqrt{-1}$, n is the number of nearest neighbors of particle i, and θ_{ikl} is angle formed by the junction of $\vec{r}_k - \vec{r}_i$ and $\vec{r}_l - \vec{r}_i$ where particle k and l are nearest neighbors of particle i. And we found that there is a strong correlation between the six-fold positional order and the motion of each particle. The particles are trapped more and less in clusters of medium-range crystalline order. While, those out of the cluster can move smoothly. The clusters have typically 10 times larger life time than the relaxation time of the liquid τ_α. Therefore it is considered that this correlation is the origin of the dynamic heterogeneity.

References

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